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MULTISTABLE CHEMICAL STEADY-STATES

by



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A THESIS

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The undersigned certify that they have read and recommend to the Faculty of Graduate Studies and Research for acceptance, a thesis entitled "MULTISTABLE CHEMICAL STEADY-STATES" submitted by CHERYL K. VAN KIRK in partial fulfillment of the requirements for the degree of Master of Science.





ABSTRACT

A recent experiment<sup>8</sup> has shown that a chemical system undergoing a reaction may exhibit spatial structure. In this experiment the reaction mixture gradually arranged itself into alternating layers of red and blue. In the blue layers the concentration of one of the species present was higher than its concentration in the red layers. This paper will discuss a possible theoretical explanation for the appearance of structure in chemical systems. It is shown that this may happen if the homogeneous steady-state solution to the chemical rate equations (including diffusion) can become unstable with respect to spontaneous spatially dependent fluctuations.

The first chapter of this paper is an introduction, including a historical summary. The second chapter defines the concepts of stability, marginal stability, and instability for homogeneous steady-state solutions. The two types of boundary conditions are discussed and a criterion is developed for each type of boundary condition to determine if a homogeneous steady-state solution is stable or not. The criterion is valid for any dimension and shape of system, provided that the surface of the system is smooth.

Next a specific example of a chemical system which can become unstable with respect to spatially dependent fluctuations is presented<sup>7</sup>. This is followed by an example which illustrates that the behavior of a system can differ depending on which type of boundary condition is imposed



on it. Following this a simple model developed by Lefever<sup>12,13,16</sup> is discussed and some numerical results are presented.

The fourth chapter is concerned with the concept of multiple-steady-state solutions to the chemical rate equations. A simple mechanism is presented and the stability of all the homogeneous steady-state solutions is studied in detail using Lefever's model. Then it is shown that a homogeneous steady-state solution can be stable simultaneously with an inhomogeneous steady-state solution.

The conclusion of this paper will discuss in more detail the laboratory experiment which confirms that spatial structure can exist in chemical systems.





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## CHAPTER 1

### INTRODUCTION

It is common to think of chemical reactions occurring in a spatially homogeneous medium - that is, the concentrations of the various chemical species are distributed uniformly throughout the reaction vessel. At thermodynamic equilibrium and in near-equilibrium situations this must be the case.<sup>14</sup> This is true because any spontaneous fluctuation which takes the system away from the homogeneous state must die out in time. Thus the system cannot evolve away from the homogeneous situation. However, in systems far from equilibrium this may not be the case. It might be that fluctuations could grow in time and the system would evolve away from the homogeneous state.

Mathematically, the study of fluctuations can be linked to the study of the stability of differential equations. For chemical systems, the appropriate differential equations are the chemical rate equations including the effect of diffusion. This problem was first studied by Turing<sup>21</sup> in 1952. In his paper, he presented several reaction mechanisms which could lead to a structured system. However, after the publication of this paper, little work was done in the chemistry field for a long time. But the general area of stability was investigated more by people in hydrodynamics<sup>2</sup>. Then in 1966 Scriven and Gmitro<sup>20</sup> published a paper recalling Turing's work and linking chemical systems to the type of work which had been done in hydrodynamics. In 1967 and 1968 Prigogine<sup>15,16</sup> and several





other people connected with him<sup>12,13</sup> published some articles along the same lines as Scriven and Gmitro's, but including an explanation of the phenomena of dissipative instability in terms of non-equilibrium thermodynamics. Since then several more articles and a book have been published.

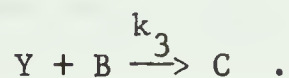
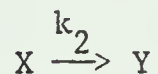
This paper continues the study of spatial structure in chemical systems. First a mathematical criterion for determining stability or lack of it is developed. This criterion is then applied to a mechanism to give a straightforward example of a dissipative instability. Then the question of the boundary conditions imposed on the system is discussed at length. This problem seems to have been ignored by most authors. However, very recent works by Ross and Ortoleva<sup>18,19</sup> have also discussed boundary behavior, although their treatment is very different from the approach taken in this paper. Following this, an example of the phenomena of multiple steady-states is presented and the stability of each state is examined. A further extension of the concept of multiple steady-states is then discussed. This part of the paper was motivated by an unsolved problem presented by Edelstein<sup>5</sup>. This extension of multiple steady-states shows for a simplified model an answer to Edelstein's problem. The general problem, as yet, remains unsolved.



## CHAPTER 2

### MATHEMATICAL PRELIMINARIES

For the rest of this work we shall be concerned about chemical systems in which the reactions are assumed to be completely known. For example, the system could be governed by the following reaction sequence or mechanism:



The overall reaction is  $A + B \rightarrow C$  . It will be assumed that the concentrations of  $A$  ,  $B$  , and  $C$  are fixed and constant in time. Then the system of differential equations (chemical rate equations) associated with this system is:

$$\frac{dX}{dt} = k_1 A - k_2 X$$

$$\frac{dY}{dt} = k_2 X - k_3 BY \quad .$$

Capital letters are used in the chemical rate equations to denote the concentration of the corresponding substance. This system has one time independent or "steady-state" solution obtained by setting





$$\frac{dX}{dt} = \frac{dY}{dt} = 0$$

and solving the resulting algebraic equations. In this case the steady-state solution is:

$$X_o = \frac{k_1 A}{k_2} \quad ; \quad Y_o = \frac{k_1 A}{k_3 B} \quad .$$

In general, for a system with  $N$  time dependent species (intermediates) we have:

$$\frac{dX_n}{dt} = f_n(X_1, X_2, \dots, X_N) \quad ; \quad n = 1, \dots, N \quad (2.1)$$

For the present we will assume there exists one steady-state solution,  $X_{10}, X_{20}, \dots, X_{N0}$  .

Let us now consider solutions that have been perturbed from the steady-state solution. These can be written as:

$$X_n(t) = X_{n0} + \bar{\psi}_n(t) \quad ; \quad n = 1, \dots, N \quad (2.2)$$

The  $\bar{\psi}_n(t)$  represent fluctuations away from the steady-state solution. These could represent Brownian motion or some other spontaneous disturbance in the system. The  $\bar{\psi}_n(0)$  are assumed to be small in comparison with  $X_{n0}$  . Physically, we would expect that a small disturbance in the system would not drastically alter the system. That is, we expect that the perturbed solutions will remain near the steady-state solutions as time increases. This will be the case if each  $\bar{\psi}_n(t) \rightarrow 0$  as  $t \rightarrow \infty$  . Then we say that the steady-state solution  $X_{n0}$  ;  $n = 1, \dots, N$  is stable. If any



$\bar{\psi}_n(t)$  becomes large in comparison to  $\bar{\psi}_n(0)$ , we will say that the steady-state solution is unstable. If none of the  $\bar{\psi}_n(t)$  become large in comparison to  $\bar{\psi}_n(0)$  and at least one of the  $\bar{\psi}_n(t)$  does not tend to zero, then we will say that the steady-state solution is marginally stable.

Let us now substitute equation (2.2) into (2.1). This gives:

$$\frac{d\bar{\psi}_n}{dt} = f_n(X_{10} + \bar{\psi}_1(t), X_{20} + \bar{\psi}_2(t), \dots, X_{N0} + \bar{\psi}_N(t)) \quad (2.3)$$

$$n = 1, \dots, N$$

We will expand the right hand side in a Taylor series and retain only terms of order  $\bar{\psi}_n(t)$ . We obtain:

$$\begin{aligned} \frac{d\bar{\psi}_n}{dt} &= f_n(X_{10}, X_{20}, \dots, X_{N0}) + \sum_{j=1}^N \left( \frac{\partial f_n}{\partial X_j} \bigg|_{X_1=X_{10}, \dots, X_N=X_{N0}} \right) \bar{\psi}_j \\ \frac{d\bar{\psi}_n}{dt} &= \sum_{j=1}^N \left( \frac{\partial f_n}{\partial X_j} \bigg|_{X_{10}, X_{20}, \dots, X_{N0}} \right) \bar{\psi}_j \end{aligned} \quad (2.4)$$

$$n = 1, \dots, N$$

We have used here the fact that the  $X_{n0}$  are the steady-state solution. Equations (2.4) are now a system of linear differential equations for the fluctuations. Provided that it was valid to retain only terms of order  $\bar{\psi}_n(t)$  (linearization of equations (2.1)), we can now solve (2.4) and find the fluctuation explicitly as functions of time and from this determine the stability of the steady-state solution. The validity of linearization



of equation (2.1) is determined by the form of the functions  $f_n$ . We will make use of the following theorem<sup>1</sup>.

Given a system of differential equations:

$$\frac{dX_n}{dt} = f_n(X_1, \dots, X_N) \quad ; \quad n = 1, \dots, N \quad (2.5)$$

such that each  $f_n$  can be written in this form:

$$f_n = \sum_{j=1}^N a_{nj} X_j + g_n(X_1, \dots, X_N) \quad ; \quad n = 1, \dots, N \quad (2.6a)$$

where the  $a_{nj}$  are constants, and such that:

$$\frac{t_{1/2} \cdot |g_n(X_1, \dots, X_N)|}{\sqrt{X_1^2 + \dots + X_N^2}} \rightarrow 0 \quad \text{as} \quad \sqrt{X_1^2 + \dots + X_N^2} \rightarrow 0 \quad ; \quad n = 1, \dots, N \quad (2.6b)$$

where  $t_{1/2}$  is the half life of the overall reaction,

then if the corresponding linearized system of differential equations is stable, system (2.5) is stable or marginally stable. If the corresponding linearized system of differential equations is unstable, system (2.5) is unstable.

We will find that in all the cases we wish to consider conditions (2.6a) and (2.6b) will be satisfied.

We are now in a position to solve equation (2.4) explicitly.

Let  $\underline{\psi}$  be the column vector whose  $n$ th element is  $\overline{\psi}_n$  and let  $\underline{A}$  be the matrix defined by





$$A_{nj} = \left. \frac{\partial f_n}{\partial X_j} \right|_{X_1=X_{10}, \dots, X_N=X_{N0}} \quad (2.7)$$

Then (2.4) can be rewritten in matrix notation as:

$$\frac{d\underline{\psi}}{dt} = \underline{A} \underline{\psi} \quad (2.8)$$

Once it is in this form it is easy to show that the solution is:

$$\underline{\psi}(t) = \underline{\psi}_0 e^{\underline{A}t} \quad .$$

Further each fluctuation  $\overline{\psi}_n$  may be expressed as:

$$\overline{\psi}_n = \sum_{j=1}^N c_{nj} e^{w_j t} \quad ; \quad n = 1, \dots, N \quad (2.9)$$

where  $c_{nj}$  is some constant amplitude and the  $w_j$  are the eigenvalue of the matrix  $\underline{A}$ . Clearly if the real part of each  $w_j$  is less than zero, each fluctuation  $\overline{\psi}_n$  will approach zero as time increases. Then the steady-state solution will be stable. However, if just one of the eigenvalues has a positive real part, the perturbation will increase in time and the steady-state solution will be unstable. If one of the  $w_j$  should have a real part equal to zero, this would correspond to the case of marginal stability. However, examples can be constructed in which the linearized system of equations is marginally stable and the corresponding nonlinear system is not. So if we find an  $w_j = 0$  we cannot conclude that the steady-state solution to a nonlinear set of chemical rate equations is marginally stable. However, a positive real part of one of the  $w_j$  would still indicate instability. Thus we see that determining the stability



of the steady-state solution for a system of chemical rate equations is equivalent to determining if the eigenvalues of the matrix A corresponding to the system have any positive real parts.

Clearly A will depend on the rate constants, and on the concentrations of the reactants and possibly the products. So the eigenvalues of A will be dependent on the same quantities and it may turn out that the system becomes unstable for some values of the rate constants and concentrations. This means that in the instability region if a fluctuation occurs, the solution to the kinetic equations will be:

$$X_n = X_{n0} + \bar{\psi}_n(t) \quad ; \quad n = 1, \dots, N$$

and this solution will go away from the steady-state solution. That is, the concentration of the  $X_n$  will become time dependent. An example of this will be considered later.

Until now we have not considered any part of our problem to be spatially dependent. Let us now allow diffusion of the intermediate species in the system. Using Fick's law of diffusion the chemical rate equations (2.1) now become:

$$\frac{\partial X_n}{\partial t} = f_n(X_1, X_2, \dots, X_N) + D_n \nabla^2 X_n \quad (2.10)$$

$$n = 1, \dots, N \quad .$$

$D_n$  is the diffusion constant of the  $n$ th intermediate species.



It should be noted that we are now considering a system of coupled partial differential equations. It will be necessary to impose boundary conditions on this system of equations. In a system with diffusion two different types of boundary conditions may be applicable depending on the experimental situation<sup>10</sup>. One is to have fixed values of the concentrations at the boundaries. An example of this is:

$$X_n(\underline{r}, t) = X_{n0} \quad \text{on } \partial S \quad ; \quad n = 1, \dots, N \quad (2.11)$$

where  $\partial S$  is the boundary of the region  $S$  in which the system under consideration is defined. This type of boundary condition is applicable if there is diffusion through the boundary, for example, with a membrane. This kind of boundary condition will be referred to as the fixed boundary condition. However, if the body which composes the boundary is insoluble in the fluid in the system and so diffusion cannot take place across the boundary, then the appropriate boundary condition is:

$$\frac{X_n}{\partial \nu} = 0 \quad \text{at the boundary; } \quad n = 1, \dots, N \quad (2.12)$$

where  $\nu$  is the unit outward normal to the surface of  $S$ . We would expect this type of boundary conditions to be applicable in most experimental situations. We will refer to this type of boundary conditions as derivative boundary conditions.

We will assume that equation (2.10) has a "steady-state homogeneous" solution obtained by solving:



$$f_n(X_1, X_2, \dots, X_N) = 0 \quad ; \quad n = 1, \dots, N \quad . \quad (2.13)$$

We will designate this solution by:

$$X_{n0} \quad ; \quad n = 1, \dots, N \quad . \quad (2.14)$$

We again wish to investigate the stability of this solution.

As before we write the perturbed solution:

$$X_n = X_{n0} + \bar{\psi}_n(\underline{r}, t) \quad ; \quad n = 1, \dots, N \quad . \quad (2.15)$$

Note that the fluctuations are now functions of  $\underline{r}$  as well as  $t$  .

Substituting (2.15) into (2.11) gives:

$$\frac{\partial \bar{\psi}_n(\underline{r}, t)}{\partial t} = f_n(X_{10} + \bar{\psi}_1, \dots, X_{N0} + \bar{\psi}_N) + D_n \nabla^2 \bar{\psi}_n \quad (2.16)$$

$$n = 1, \dots, N \quad .$$

Again we expand in a Taylor series keeping only terms linear in  $\bar{\psi}_n(\underline{r}, t)$  .

We obtain:

$$\frac{\partial \bar{\psi}_n(\underline{r}, t)}{\partial t} = \sum_{j=1}^N \left( \left. \frac{\partial f_n}{\partial X_j} \right|_{X_1=X_{10}, \dots} \right) \bar{\psi}_j + D_n \nabla^2 \bar{\psi}_n \quad . \quad (2.17)$$

We will now need to examine what effect each type of boundary condition will have on the perturbations. First we will consider the fixed boundary condition. Since the  $X_{n0}$  ,  $n = 1, \dots, N$  are solutions we must have that:





$$X_n = X_{n0} + \bar{\psi}_n(\underline{r}, t) = X_{n0} \quad \text{on} \quad \partial S \quad ; \quad n = 1, \dots, N \quad .$$

Thus:

$$\bar{\psi}_n(\underline{r}, t) = 0 \quad \text{on} \quad \partial S \quad ; \quad n = 1, \dots, N \quad .$$

It has been shown<sup>6</sup> that the eigenfunctions  $\mu_k$  of the following problem form a complete orthonormal set over the region  $S$ , provided that  $\partial S$  is a smooth surface:

$$\nabla^2 \mu_k(\underline{r}) = -k^2 \mu_k(\underline{r}) \quad ; \quad \mu_k = 0 \quad \text{on} \quad \partial S \quad . \quad (2.18)$$

We should note that  $k = 0$  is not an allowed eigenvalue for this problem. To show this let us assume it is an eigenvalue. Then there is an eigenfunction  $\mu_0$  satisfying the following:

$$\nabla^2 \mu_0 = 0 \quad ; \quad \mu_0 = 0 \quad \text{on} \quad \partial S \quad . \quad (2.19)$$

By definition an eigenfunction is not identically equal to zero. However the function  $\mu \equiv 0$  does satisfy (2.19) and by uniqueness it is the only solution. Thus there can be no eigenfunction  $\mu_0$  and zero is not an eigenvalue. We also see from (2.18) that no  $\mu_k(\underline{r})$  can be identically a constant, because it would not satisfy the boundary condition on  $\partial S$ .

We will now expand each perturbation  $\bar{\psi}_n(\underline{r}, t)$  in a series of the  $\mu_k(\underline{r})$ . We write

$$\bar{\psi}_n(\underline{r}, t) = \sum_{\ell, \ell \neq 0} b_{n\ell}(t) \mu_\ell(\underline{r}) \quad ; \quad n = 1, \dots, N \quad . \quad (2.20)$$



The summation is over the allowed eigenvalues corresponding to equation (2.18) in the region  $S$ .

Now we will substitute equation (2.20) into equation (2.17) and obtain:

$$\sum_{\ell, \ell \neq 0} \mu_{\ell}(\underline{r}) \frac{\partial b_{n\ell}(t)}{\partial t} = \sum_{\ell, \ell \neq 0} \sum_{j=1}^N \left( \left. \frac{\partial f_n}{\partial X_j} \right|_{X_1=X_{10}, \dots} \right) \mu_{\ell}(\underline{r}) b_{j\ell}(t) - D_n \sum_{\ell, \ell \neq 0} \ell^2 b_{n\ell}(t) \mu_{\ell}(\underline{r}) \quad (2.21)$$

$$n = 1, \dots, N.$$

Now we multiply both sides of equation (2.21) by  $\mu_k(\underline{r})$  and then integrate each side over the region  $S$ . Using the orthonormality of the  $\mu_k(\underline{r})$  we obtain:

$$\begin{aligned} \frac{\partial b_{nk}(t)}{\partial t} &= \sum_{j=1}^N \left( \left. \frac{\partial f_n}{\partial X_j} \right|_{X_1=X_{10}, \dots} \right) b_{jk}(t) - D_n k^2 b_{nk}(t) \\ &= \sum_{j=1}^N \left[ \left( \left. \frac{\partial f_n}{\partial X_j} \right|_{X_1=X_{10}, \dots} - D_n k^2 \delta_{nj} \right) b_{jk} \right] \end{aligned} \quad (2.23)$$

$$n = 1, \dots, N.$$

Equation (2.23) is now a linear system of differential equations for the  $b_{nk}(t)$ . It is similar in form to equation (2.4). In analogy with (2.7) we can define a matrix  $\underline{\underline{A}}'(k)$  and write this expression for the  $n$ th



element:

$$A'_{nj}(k) = \left. \frac{\partial f_n}{\partial X_j} \right|_{X_1=X_{10}, \dots, X_N=X_{N0}} - D_n k^2 \delta_{nj} \quad (2.24)$$

Then, similar to equation (2.9), we can write:

$$b_{nk}(t) = \sum_{j=1}^N c'_{nj} e^{w'_j(k)t} ; \quad n = 1, \dots, N \quad (2.25)$$

where the  $c'_{nj}$  are constant amplitudes and the  $w'_j$  are the eigenvalues of the matrix  $\underline{\underline{A}}'(k)$ . So now we may write the fluctuation as:

$$\begin{aligned} \bar{\psi}_n(\underline{r}, t) &= \sum_{k \neq 0, k} b_{nk}(t) \mu_k(\underline{r}) \\ &= \sum_{k \neq 0, k} \sum_{j=1}^N c'_{nj} e^{w'_j(k)t} \mu_k(\underline{r}) \end{aligned} \quad (2.26)$$

$n = 1, \dots, N$  .

Again, it is evident that whether the fluctuations will grow in time or die out depends on whether any of the eigenvalues of  $\underline{\underline{A}}'(k)$  possess positive real parts or not.

For the case of the boundary conditions given by (2.13) we may show that a similar analysis will go through. We require that the solution given by (2.15) satisfy the boundary condition. That is:

$$\frac{\partial X_n}{\partial v} = 0 = \frac{\partial}{\partial v} (X_{n0} + \bar{\psi}_n(\underline{r}, t)) \quad \text{on } \partial S ; \quad n = 1, \dots, N \quad (2.27)$$





Thus:

$$\frac{\partial \bar{\psi}_n}{\partial \nu}(\underline{r}, t) = 0 \quad \text{on} \quad \partial S, \quad n = 1, \dots, N. \quad (2.28)$$

In analogy with problem (2.18) it has been shown<sup>6</sup> that the eigenfunctions  $V_k$  of the following problem form a complete orthonormal set in the region  $S$ .

$$\nabla^2 V_k(\underline{r}) = -k^2 V_k(\underline{r}) \quad ; \quad \frac{\partial V_k}{\partial \nu} = 0 \quad \text{on} \quad \partial S. \quad (2.29)$$

It should be noted that in this case zero is an eigenvalue with eigenfunction  $V_0$  identically equal to a constant. As before, we expand each perturbation in a series of the  $V_k$ :

$$\bar{\psi}_n(\underline{r}, t) = \sum_{\ell} d_{n\ell}(t) V_k(\underline{r}). \quad (2.30)$$

Now we can continue exactly as before and we will obtain the following result:

$$\bar{\psi}_n(\underline{r}, t) = \sum_k \sum_{j=1}^N c'_{nj} e^{w'_j(t)} V_k(\underline{r}). \quad (2.31)$$

From equations (2.26) and (2.31) we see that we obtain very similar results for both types of boundary conditions. However, in (2.26) (corresponding to fixed boundary conditions) the summation does not include  $k = 0$ . Also no  $\mu_k(\underline{r})$  can be identically equal to a constant which means that homogeneous perturbations are forbidden. On the other hand, in (2.31) (corresponding to derivative boundary conditions) the zero eigenvalue is allowed and the corresponding eigenfunction is a constant. Thus homogeneous



perturbations are allowed. The importance of this difference will be made clearer later on in this paper.

The above arguments are valid for any dimension and any shape of system, provided that it has smooth boundaries. The matrix  $\underline{A}'$  will be the same in all cases. For simplicity, we shall work with one dimensional systems in the rest of this paper. In this case the functions  $\mu_k$  and  $V_k$  would correspond to  $\sin kr$  and  $\cos kr$  respectively, where  $k = \frac{\ell\pi}{L}$ ,  $L$  is the length of the interval, the  $\ell$  are integers, including zero for  $\cos kr$ .

Thus we see from equation (2.15) that if the homogeneous steady-state solution is unstable and fluctuations do not regress in time, then the system may evolve into a solution that depends on the space parameter  $r$ . This would mean that the concentrations of the intermediate species would not be homogeneous in space. So this is one way that a chemical system could exhibit an inhomogeneous state.

It is clear that we would be greatly aided if we had a relatively simple method for determining if any of the eigenvalues of a matrix have a positive real part or not. Fortunately there exists a criterion known as the "Routh-Hurwitz" conditions<sup>4</sup> which do this. We will now briefly explain them.

To find the eigenvalues of the matrix  $A$  we need to consider the following equation:



$$\begin{vmatrix} w-A_{11} & -A_{12} & -A_{13} & \cdots \\ -A_{21} & w-A_{22} & -A_{23} & \cdots \\ -A_{31} & -A_{32} & w-A_{33} & \cdots \\ \vdots & \vdots & \vdots & \ddots \end{vmatrix} = 0 \quad (2.31)$$

For an  $N \times N$  matrix  $\underline{A}$  this can be rewritten as a polynomial of degree  $N$  or a "dispersion equation":

$$w^N + a_1 w^{N-1} + a_2 w^{N-2} + \cdots + a_{N-1} w + a_N = 0 \quad (2.32)$$

The Routh-Hurwitz conditions are inequalities among the coefficients  $a_1, \dots, a_N$  of the polynomial. It is necessary and sufficient that they all be satisfied in order that the real part of every eigenvalue of  $\underline{A}$  be negative. Because these conditions are necessary, it follows immediately that if one or more of them is violated, then the real part of at least one eigenvalue is positive. For future use the Routh-Hurwitz conditions for polynomials of degree two, three, and four are given below<sup>4</sup>:

<u>Polynomial</u>	<u>Routh-Hurwitz Conditions</u>
$w^2 + a_1 w + a_2$	$a_2 > 0, a_1 > 0$
$w^3 + a_1 w^2 + a_2 w + a_3$	$a_3 > 0, a_1 > 0, a_1 a_2 > a_3$
$w^4 + a_1 w^3 + a_2 w^2 + a_3 w + a_4$	$a_4 > 0, a_2 > 0, a_1 > 0$
	$a_3(a_1 a_2 - a_3) > a_1^2 a_4 \quad (2.33)$

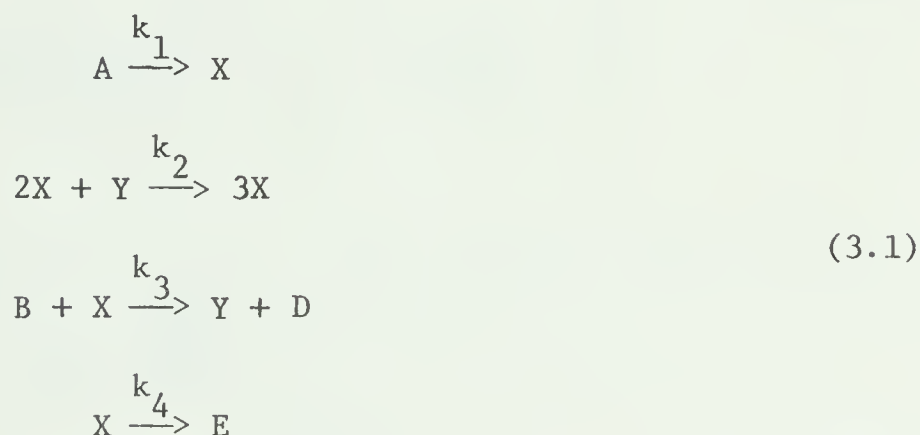


## CHAPTER 3

### SPECIFIC EXAMPLES

#### Part I

To begin this section we will do a simple example to illustrate the theory developed in the previous chapter. We will consider the following mechanism<sup>7</sup>:



The overall reaction is  $A + B \rightarrow D + E$ . We have set the rate constants for all back reactions equal to zero, so that the system is infinitely far from equilibrium. It would be possible to allow the back reactions<sup>6</sup>, although it would complicate the algebra substantially. It should also be noted that this mechanism contains a trimolecular step. While not realistic, it is again simpler.

In writing out the chemical rate equations we shall at first neglect diffusion and work only with the possibility of a temporal instability. The chemical rate equations are:





$$\frac{dX}{dt} = k_1 A + k_2 X^2 Y - k_3 BX - k_4 X \quad (3.2)$$

$$\frac{dY}{dt} = k_3 BX - k_2 X^2 Y \quad .$$

There is one steady-state solution which is obtained by solving:

$$k_1 A + k_2 X^2 Y - k_3 BX - k_4 X = 0 \quad (3.3)$$

$$k_3 BX - k_2 X^2 Y = 0 \quad .$$

This solution is given by:

$$X_0 = \frac{k_1 A}{k_4} \quad (3.4)$$

$$Y_0 = \frac{k_3 k_4 B}{k_1 k_2 A} \quad .$$

Now we shall investigate the stability of the steady-state solution. We shall use equation (2.7) to find the matrix  $\underline{\underline{A}}$ . From the chemical rate equations we have that:

$$f_1 = k_1 A + k_2 X^2 Y - k_3 BX - k_4 X \quad (3.5)$$

$$f_2 = k_3 BX - k_2 X^2 Y \quad .$$



So from equation (2.7) we obtain:

$$A_{11} = \frac{\partial f_1}{\partial X} \Big|_{X_0, Y_0} = 2k_2 X_0 Y_0 - k_3 B - k_4 \quad . \quad (3.6)$$

The other matrix elements are found in a similar manner. Using equation (3.4) we have that:

$$\underline{\underline{A}} = \begin{pmatrix} k_3 B - k_4 & k_2 \left( \frac{k_1 A}{k_4} \right)^2 \\ -k_3 B & -k_2 \left( \frac{k_1 A}{k_4} \right)^2 \end{pmatrix} \quad (3.7)$$

We now need to find the eigenvalues of  $\underline{\underline{A}}$ . From equation (2.31) we can immediately write this equation for the eigenvalues of  $\underline{\underline{A}}$ :

$$\begin{vmatrix} w - k_3 B + k_4 & -k_2 \left( \frac{k_1 A}{k_4} \right)^2 \\ k_3 B & w + k_2 \left( \frac{k_1 A}{k_4} \right)^2 \end{vmatrix} = 0 \quad (3.8)$$

The resulting dispersion equation is:

$$w^2 + w \left( k_2 \left( \frac{k_1 A}{k_4} \right)^2 + k_4 - k_3 B \right) + k_4 k_2 \left( \frac{k_1 A}{k_4} \right)^2 = 0 \quad . \quad (3.9)$$

We may now use the Routh-Hurwitz conditions (2.33) for a second degree polynomial to check if it is possible to have an instability. We have:



$$a_2 = k_4 k_2 \left( \frac{k_1 A}{k_4} \right)^2 \quad (3.10a)$$

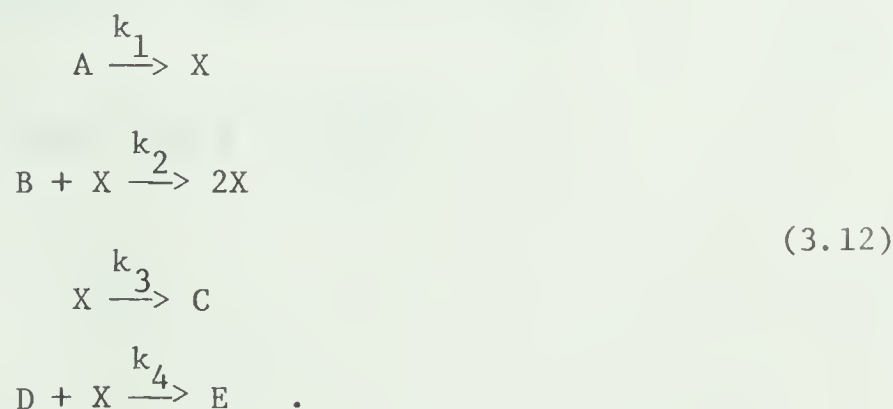
$$a_1 = k_2 \left( \frac{k_1 A}{k_4} \right)^2 + k_4 - k_3 B \quad (3.10b)$$

It is obvious that  $a_2 > 0$  for all physically meaningful values of the rate constants and  $A$ . However  $a_1$  is not greater than zero for all reasonable values. We see that there exists a critical value of  $B$ , call it  $B_c$ , such that for  $B > B_c$ ,  $a_1 < 0$ . This critical value is given by:

$$B_c = \frac{k_2}{k_3} \left( \frac{k_1 A}{k_4} \right)^2 + \frac{k_4}{k_3} \quad (3.11)$$

Thus for  $B > B_c$ , the steady-state solution to the chemical rate equations (3.2) becomes unstable. It can be expected that if it is possible the system will evolve to a time dependent solution for  $B > B_c$ .

It may be noted that the chemical rate equations (3.2) are non-linear. This will, in general, be the case if we wish to find a meaningful instability in the chemical rate equation. A simple example will show why linear equations would be unsatisfactory. Consider the following mechanism:







It is convenient to set all rate constants equal to one. The chemical rate equation is:

$$\frac{dX}{dt} = A + (B-1-D)X \quad . \quad (3.13)$$

We have

$$X_0 = \frac{A}{B-1-D} \quad . \quad (3.14)$$

The matrix A in this case consists of the single element (B-1-D) . The condition for instability is  $B < 1 + D$  . However, we see from equation (3.14) that when the instability condition holds, the steady-state solution is negative which does not make sense physically. Similar phenomena appear to happen in systems which contain more than one intermediate species and have linear chemical rate equations.

Now we shall demonstrate the existence of an instability that results from fluctuations which depend on both time and space parameters. We again consider mechanism (3.1) but this time in the chemical rate equations we allow for diffusion<sup>7,14,16</sup> . We have:

$$\begin{aligned} \frac{\partial X}{\partial t} &= k_1 A + k_2 X^2 Y - k_3 B X - k_4 X + D_x \frac{\partial^2 X}{\partial r^2} \\ \frac{\partial Y}{\partial t} &= k_3 B X - k_2 X^2 Y + D_y \frac{\partial^2 Y}{\partial r^2} \quad . \end{aligned} \quad (3.15)$$



The steady-state homogeneous solution is still given by equations (3.4). This time, however, in considering the stability of this solution we must use the matrix  $\underline{\underline{A}}'(k)$  whose elements are given by equation (2.24).  $f_1$  and  $f_2$  are still given by equations (3.5) and (3.6) respectively. We easily obtain for  $\underline{\underline{A}}'(k)$ :

$$\underline{\underline{A}}' = \begin{pmatrix} k_3 B - k_4 - k^2 D_x & k_2 \left( \frac{k_1 A}{k_4} \right)^2 \\ -k_3 B & -k_2 \left( \frac{k_1 A}{k_4} \right)^2 - k^2 D_y \end{pmatrix} \quad (3.16)$$

The corresponding equation for  $w$  is:

$$\begin{vmatrix} w - k_3 B + k_4 + k^2 D_x & -k_2 \left( \frac{k_1 A}{k_4} \right)^2 \\ k_3 B & w + k_2 \left( \frac{k_1 A}{k_4} \right)^2 + k^2 D_y \end{vmatrix} = 0 \quad (3.17)$$

This may be rewritten as:

$$\begin{aligned} w^2 + w(k_4 + k_2 \left( \frac{k_1 A}{k_4} \right)^2 - k_3 B + k^2 D_x + k^2 D_y) \\ + k_4 k_2 \left( \frac{k_1 A}{k_4} \right)^2 + k^2 D_x k_2 \left( \frac{k_1 A}{k_4} \right)^2 - k^2 k_3 B D_y \\ + k^2 k_4 D_y + k^4 D_x D_y = 0 \end{aligned} \quad (3.18)$$



For algebraic simplicity we shall at this point set all rate constants equal to one. Then equation (3.18) becomes:

$$\begin{aligned} w^2 + w(1 + A^2 - B^2 + k^2 D_x + k^2 D_y) \\ + A^2 + k^2 A^2 D_x - k^2 B D_y + k^2 D_y + k^4 D_x D_y = 0 \end{aligned} \quad (3.19)$$

The Routh-Hurwitz stability condition of  $a_1 > 0$  gives us the following critical value of  $B$  :

$$B_c = 1 + A^2 + k^2 (D_x + D_y) \quad (3.20)$$

When  $B > B_c$ , the homogeneous steady-state solution will become unstable. However, it is now possible to violate the condition that  $a_2 > 0$ . This gives us another critical  $B$  which we will denote by  $B'_c$  :

$$B'_c(k) = \left( \frac{A^2}{k^2 D_y} + \frac{D_x A^2}{D_y} + 1 + k^2 D_x \right) \quad (3.21)$$

It is of interest to find which value of  $k$  gives the smallest  $B'_c$ . To find this we differentiate  $B'_c$  with respect to  $k^2$  and set the resulting expression equal to zero. We obtain the following equation:

$$\frac{A^2}{D_y} - k^4 D_x = 0 \quad (3.22)$$

This is easily solved to yield:

$$k_c^2 = \frac{A}{(D_x D_y)^{1/2}} \quad (3.23)$$



Putting this value into equation (3.21) yields:

$$B'_c = \left( 1 + \left( \frac{D_x}{D_y} \right)^{\frac{1}{2}} A \right)^2 . \quad (3.24)$$

At this point, Prigogine<sup>7</sup> who developed this theory concludes by stating that for  $B$  greater than the minimum of  $B_c$  and  $B'_c$ , the homogeneous steady-state solution becomes unstable. The critical value of  $B$  corresponds to a "symmetry breaking transition". If beyond the instability, a space dependent state exists, Prigogine calls it a "dissipative structure".

However, it is interesting to examine more closely the role the boundary conditions may play. First let us consider the derivative boundary conditions. For this case we have:

$$\left. \frac{\partial X(r,t)}{\partial r} \right|_{r=0} = \left. \frac{\partial X(r,t)}{\partial r} \right|_{r=L} = 0 \quad (3.25)$$

$$\left. \frac{\partial Y(r,t)}{\partial r} \right|_{r=0} = \left. \frac{\partial Y(r,t)}{\partial r} \right|_{r=L} = 0 .$$

With this type of boundary condition it was shown previously that it is possible to have a perturbation independent of  $r$ . That is, we may have:

$$\begin{aligned} X &= X_0 + \bar{\psi}(t) \\ Y &= Y_0 + \bar{\phi}(t) . \end{aligned} \quad (3.26)$$





This homogeneous perturbation corresponds, of course, to  $k = 0$ . At  $k = 0$ ,  $B_c$  takes on its minimum value which is:

$$B_c(\min) = 1 + A^2. \quad (3.27)$$

If the values of  $D_x$  and  $D_y$  are such that:

$$B_c(\min) = 1 + A^2 < B'_c = \left[ 1 + \left( \frac{D_x}{D_y} \right)^{\frac{1}{2}} A \right]^2 \quad (3.28)$$

then the instability will always be caused first by a homogeneous perturbation such as in (3.26). Initially the system will go into a time dependent, space independent solution.

On the other hand, if the boundary conditions are of the other type, that is:

$$X(r,t) \Big|_{r=0} = X(r,t) \Big|_{r=L} = X_0 \quad (3.29)$$

$$Y(r,t) \Big|_{r=0} = Y(r,t) \Big|_{r=L} = Y_0$$

a different situation exists. For these boundary conditions, perturbations of the form of (3.26) are impossible to have. Since we cannot have perturbations which correspond to  $k = 0$ ,  $B_c$  will take on its minimum value when  $k^2$  is the smallest possible. Since the eigenfunctions  $\mu_k$  are  $\sin kr$ , this means when  $k = \frac{\pi}{L}$ . In this case we have that:



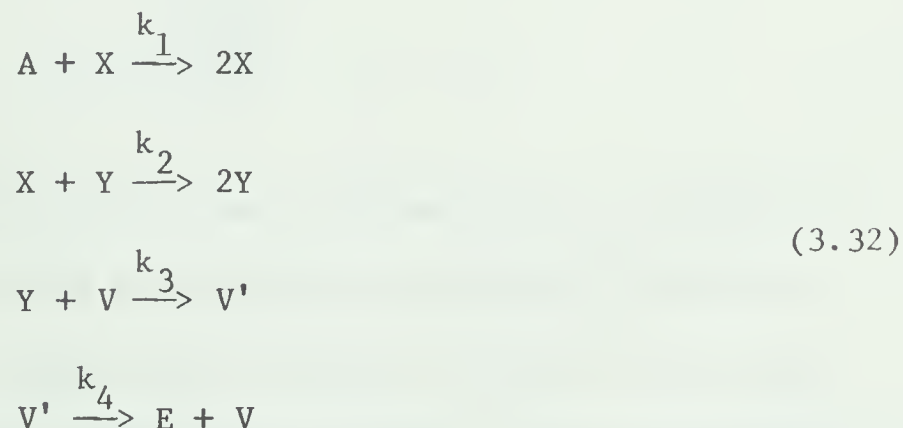
$$B_c = 1 + A^2 + (D_x + D_y) \frac{\pi^2}{L^2} \quad . \quad (3.30)$$

The instability will be caused by whichever is the smaller:

$$1 + A^2 + (D_x + D_y) \frac{\pi^2}{L^2} \quad \text{or} \quad B'_c = [1 + \left( \frac{D_x}{D_y} \right)^{\frac{1}{2}} A]^2 \quad . \quad (3.31)$$

However, no matter whether  $B_c$  or  $B'_c$  is the smaller, the fluctuation must be inhomogeneous and beyond the instability the system evolves into a space dependent state.

Thus we see that there is a fundamental difference between the two types of boundary conditions. With one of them, homogeneous perturbations are allowed and with the other homogeneous perturbations are not allowed. The importance of this difference is made clearer by a consideration of the following mechanism. Prigogine<sup>7</sup> has stated, without proof, that this mechanism may exhibit a symmetry breaking transition. The mechanism is:



The overall reaction is  $A \rightarrow E$  . The chemical rate equations for this system are:



$$\frac{\partial X}{\partial t} = AX - k_2 XY + D_x \frac{\partial^2 X}{\partial r^2} \quad (3.33a)$$

$$\frac{\partial Y}{\partial t} = k_2 XY - k_3 YV + D_y \frac{\partial^2 Y}{\partial r^2} \quad (3.33b)$$

$$\frac{\partial V}{\partial t} = k_4 V' - k_3 YV + D_v \frac{\partial^2 V}{\partial r^2} \quad (3.33c)$$

$$\frac{\partial V'}{\partial t} = k_3 YV - k_4 V' + D_{v'} \frac{\partial^2 V'}{\partial r^2} \quad . \quad (3.33d)$$

Since the product  $k_1 A$  always occurs together, it is convenient to denote it simply by  $A$ . This convention will always be followed where applicable in the remainder of this paper.

The homogeneous steady-state solution to the system of equations (3.33) is:

$$\begin{aligned} X_0 &= \frac{k_4 V'_0}{A} \\ Y_0 &= \frac{A}{k_2} \\ V_0 &= \frac{k_4 k_2 V'_0}{k_3 A} \quad . \end{aligned} \quad (3.34)$$

$V'_0$  is an arbitrary parameter which arises because the set of algebraic equations of which (3.34) is the solution has two linearly dependent equations. (See equations (3.33c) and (3.33d)). We wish to test the stability of this homogeneous steady-state solution. Using equations (2.24) and (2.31) we easily obtain the following equation:



$$\begin{vmatrix}
 w + k^2 D_x & \frac{k_2 k_4 V'_0}{A} & 0 & 0 \\
 \frac{-k_3 A}{k_2} & w + k^2 D_y & \frac{k_3 A}{k_2} & 0 \\
 0 & \frac{k_2 k_4 V'_0}{A} & w + \frac{k_3 A}{k_2} + k^2 D_v & -k_4 \\
 0 & \frac{-k_2 k_4 V'_0}{A} & \frac{-k_3 A}{k_2} & w + k_4 + k^2 D'_v
 \end{vmatrix} = 0 \quad (3.35)$$

It is easier to see what is occurring if we denote groups of constants in the following way:

$$\begin{aligned}
 \frac{k_3 A}{k_2} &= K & ; & & k^2 D_y &= b \\
 \frac{k_2 k_4 V'_0}{A} &= B & ; & & k^2 D_v &= c \\
 k^2 D_x &= a & ; & & k^2 D'_v &= d .
 \end{aligned} \quad (3.36)$$

Now equation (3.35) can be written as:

$$\begin{vmatrix}
 w + a & B & 0 & 0 \\
 -A & w + b & K & 0 \\
 0 & B & w + K + c & -k_4 \\
 0 & -B & -K & w + k_4 + d
 \end{vmatrix} = 0 \quad (3.37)$$





Expanding and simplifying gives us:

$$\begin{aligned}
 & w^4 + w^3(K + c + k_4 + d + b+a) + w^2(aK + ac + ak_4 + ad + Kd) \\
 & + w^2(ck_4 + cd + AB + bK + bc + bk_4 + bd - KB) \\
 & + w(aKd + ack_4 + acd + abK + abc + abk_4 + abd \\
 & + ABK + ABc + ABk_4 + ABd + BKd + bck_4 + bcd - aKB) \\
 & + abKd + abck_4 + abcd - aKBd + ABKd + ABck_4 + ABcd = 0 \quad . \quad (3.38)
 \end{aligned}$$

Let us consider first the derivative boundary conditions. In this case, as shown above, we must allow for homogeneous perturbations. That is;

$$a = b = c = d = 0 \quad . \quad (3.39)$$

In this case equation (3.42) simplifies considerably. It becomes:

$$w^4 + w^3(K+k_4) + w^2(AB-KB) + w(ABk_4 + ABK) = 0 \quad . \quad (3.40)$$

We immediately see that one solution is  $w = 0$  . Factoring this out leaves us with:

$$w^3 + w^2(K+k_4) + w(AB-KB) + ABk_4 + ABK = 0 \quad . \quad (3.41)$$

Now we apply the Routh-Hurwitz condition for stability to equation (3.41).

The condition that  $a_1 a_2 > a_3$  becomes:



$$(K+k_4)(AB-KB) > AB(K+k_4) \quad (3.42)$$

or:

$$A - K > A \quad (3.43)$$

In terms of the natural parameters of the system this is:

$$A - \frac{k_3 A}{k_2} > A \quad \text{or} \quad 1 - \frac{k_3}{k_2} > 1 \quad (3.44)$$

Quite obviously, this can never be satisfied since  $k_3$  and  $k_4$  must both be positive. This means that with respect to homogeneous perturbations the homogeneous steady-state solution is always unstable for all values of the rate constants and concentrations of  $A$  and  $V'_0$ . Clearly a symmetry breaking transition is not possible under the derivative boundary conditions, since the steady-state homogeneous solution is never stable.

Now we will consider for fixed boundary conditions the stability of the steady-state homogeneous solution given by equations (3.34). In this case it is easy to show that there do exist values of the rate constants, concentrations, diffusion constants, and box size such that the homogeneous steady-state solution is stable to all allowed fluctuations. As an example, choose the rate constants,  $A$  and  $V'_0$  such that  $K = 1$  and  $B = 1$ . In addition choose all of the diffusion constants equal to one and choose the size of the box to be  $\pi$ . This makes the smallest allowed  $k$  value equal to one. Then it is quite easy to show that all of the Routh-Hurwitz conditions for stability will hold in this case for any allowed fluctuations. On the other hand, it is also possible to show that for other values of the



parameters a symmetry breaking transition is possible. Let us consider the Routh-Hurwitz condition  $a_4 > 0$  and show that this may be violated under certain conditions. For convenience, we will set all rate constants equal to one. Then using (3.38) we have:

$$K = A \quad ; \quad B = \frac{V'_0}{A} \quad (3.45)$$

$$\begin{aligned} a_4 = & k^6 (D_x D_y D'_v A + D_x D_y D_v + D_x D_y D'_v k^2) \\ & + V'_0 k^2 (A D'_v + D_v + k^2 D'_v (D_v - D_x)) \quad . \end{aligned} \quad (3.46)$$

Equations (3.36) have also been used to obtain the above equations. If  $a_4 < 0$  we know that the homogeneous steady-state solution is unstable. That is, if:

$$V'_0 < \frac{-k^4 (D_x D_y D'_v D_v k^2 + D_x D_y D'_v A + D_x D_y D_v)}{[A D'_v + D_v + k^2 D'_v (D_v - D_x)]} \quad (3.47)$$

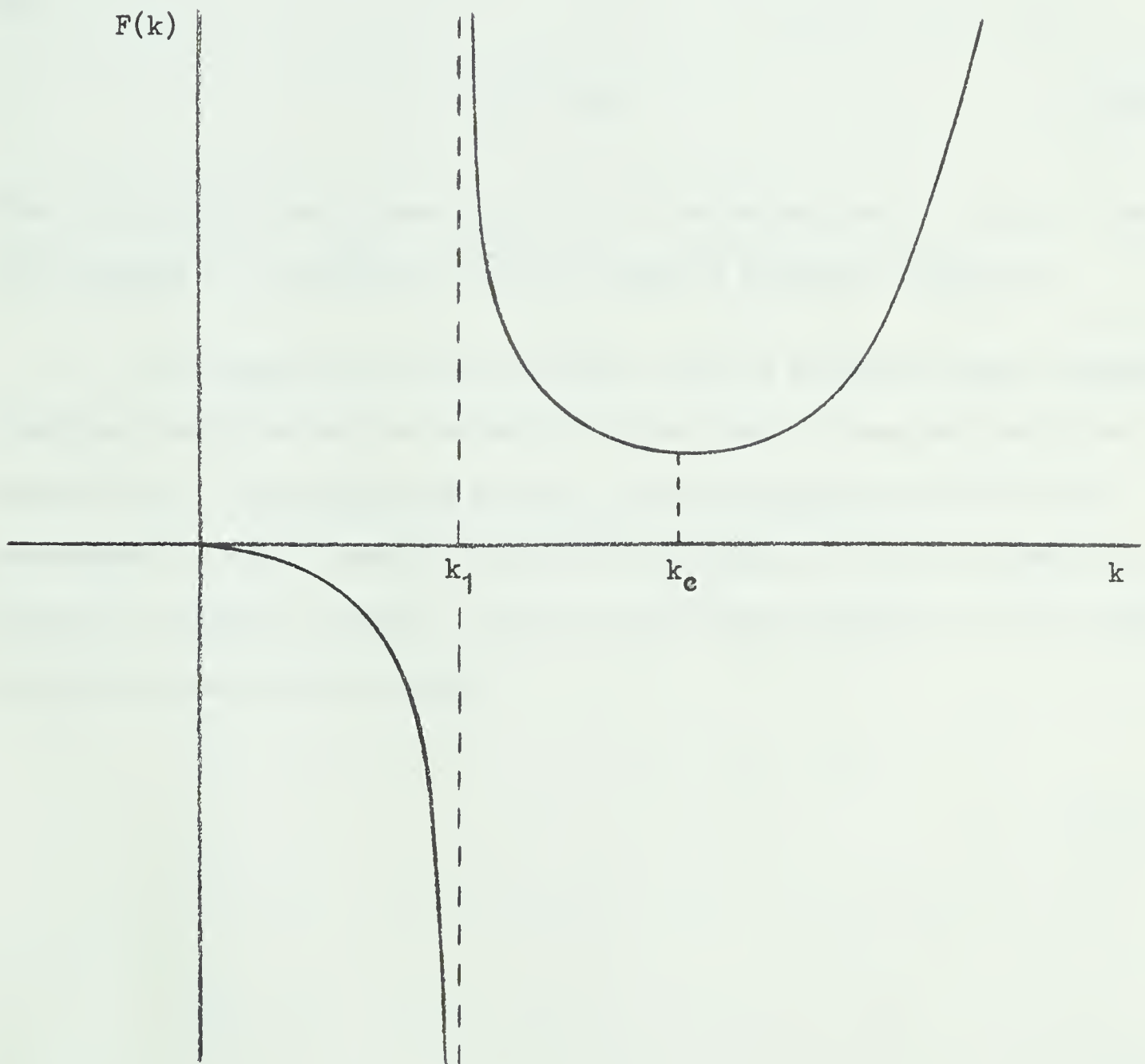
for the denominator positive. If the denominator is negative (which implies  $D_x > D_v$ ) we have the following condition for instability:

$$V'_0 > \frac{-k^4 (D_x D_y D'_v D_v k^2 + D_x D_y D'_v A + D_x D_y D_v)}{[A D'_v + D_v + k^2 D'_v (D_v - D_x)]} = F(k) \quad . \quad (3.48)$$

The right hand side of (3.47) is negative, so it would be impossible for  $V'_0$  to satisfy this. However for certain  $k, V'_0$  can satisfy (3.48). It is instructive to consider a rough sketch of  $F(k)$ . (See Figure 1.) The region where  $k < k_1$  corresponds to equation (3.47). The value of  $k_c$



FIGURE 1







can be found by differentiating  $F(k)$  with respect to  $k$  and setting the resulting expression equal to zero. Solving this equation will give  $k_c$ . If we substitute for  $k$  by  $k_c$  into  $F(k)$  given by (3.48) we have the minimum value that  $V'_0$  must be greater than in order that the steady-state homogeneous equation be unstable. That is, instability occurs if:

$$V'_0 > F(k_c) \quad . \quad (3.49)$$

Thus for boundary conditions that fix the concentrations of  $X, Y, V, V'$  on the boundary it is possible to have a symmetry breaking transition.

In summary we see that whether or not a system can have a symmetry breaking transition may be determined by the type of boundary conditions imposed on it. The mechanism we have just investigated exhibited this phenomenon for fixed concentrations at the boundary, but did not when the boundary conditions required only that the normal derivative of the concentrations vanish at the boundary.



## Part II

The chemical rate equations are, in general, a set of coupled, non-linear, partial differential equations. It would usually be difficult to study the actual time dependent, space dependent solution to this set of equations. For this reason, Lefever<sup>12,13,16</sup> has devised a model which simplifies the analysis. We will examine this model for the mechanism given by (3.1). We assume that the reaction takes place in two identical boxes labelled one and two. The concentrations of A, B, D, and E are fixed and are the same in both boxes. The concentrations of X in box 1, denoted by  $X_1$ , is constant but need not equal  $X_2$ . A similar situation is true for  $Y_1$  and  $Y_2$ . X and Y are allowed to diffuse between the two boxes.

The chemical rate equations for this model are:

$$\begin{aligned}\frac{dX_1}{dt} &= A + k_2 X_1^2 Y_1 - BX_1 - k_4 X_1 + D_x (X_2 - X_1) \\ \frac{dX_2}{dt} &= A + k_2 X_2^2 Y_2 - BX_2 - k_4 X_2 + D_x (X_1 - X_2) \\ \frac{dY_1}{dt} &= BX_1 - k_2 X_1^2 Y_1 + D_y (Y_2 - Y_1) \\ \frac{dY_2}{dt} &= BX_2 - k_2 X_2^2 Y_2 + D_y (Y_1 - Y_2) \quad .\end{aligned}\tag{3.50}$$

Note that equations (3.50) are ordinary differential equations, not partial. This is why this model is simpler to consider.



The homogeneous steady-state solution is:

$$\begin{aligned} X_{10} &= X_{20} = \frac{A}{k_4} \\ Y_{10} &= Y_{20} = \frac{k_4 B}{k_2 A} \end{aligned} \quad (3.51)$$

The inhomogeneous steady-state solution is any  $X_{10}$  ,  $X_{20}$  ,  $Y_{10}$  ,  $Y_{20}$  which satisfy the following algebraic equations:

$$\begin{aligned} A + k_2 X_{10}^2 Y_{10} - BX_{10} - k_4 X_{10} + D_x (X_{20} - X_{10}) &= 0 \\ A + k_2 X_{20}^2 Y_{20} - BX_{20} - k_4 X_{20} + D_x (X_{10} - X_{20}) &= 0 \\ BX_{10} - k_2 X_{10}^2 Y_{10} + D_y (Y_{20} - Y_{10}) &= 0 \\ BX_{20} - k_2 X_{20}^2 Y_{20} + D_y (Y_{10} - Y_{20}) &= 0 \end{aligned} \quad (3.52)$$

and

$$X_{10} \neq X_{20} \quad ; \quad Y_{10} \neq Y_{20} \quad .$$

In order to be able to study the stability of both homogeneous and inhomogeneous solutions to equations (3.50), Lefever chose all rate constants equal to one and:

$$D_x = 1 \quad ; \quad A = 2 \quad . \quad (3.53)$$

Doing this will leave us with only  $D_y$  and  $B$  as arbitrary parameters.



Let us consider first the stability of the homogeneous steady-state solution. We could use equations (2.7) and (2.31) to give us a  $4 \times 4$  matrix  $\underline{\underline{A}}$  and thus a fourth order dispersion equation to analyze. However, it is possible to consider instead two matrices, each of which is  $2 \times 2$ . First we will consider only homogeneous perturbations to the homogeneous solution. That is:

$$\begin{aligned} X_i &= X_{i0} + \bar{\psi}(t) \quad ; \quad i = 1, 2 \\ Y_i &= Y_{i0} + \bar{\phi}(t) \quad ; \quad i = 1, 2 \end{aligned} \quad (3.54)$$

Solution (3.54) is slightly different from the perturbed solution considered in chapter 2. Here the fluctuations are not completely general. Instead we have set:

$$\bar{\psi}_1(t) = \bar{\psi}_2(t) = \bar{\psi}(t) \quad \text{and} \quad \bar{\phi}_1(t) = \bar{\phi}_2(t) = \bar{\phi}(t) \quad .$$

Thus we have  $X_2 - X_1 = 0$  and  $Y_2 - Y_1 = 0$ . Substituting equations (3.54) into (3.50) and linearizing gives the following set of equations:

$$\frac{d\bar{\psi}(t)}{dt} = (B-1) \bar{\psi}(t) + 4\bar{\phi}(t) \quad (3.55)$$

$$\frac{d\bar{\phi}(t)}{dt} = B\bar{\psi}(t) - 4\bar{\phi}(t) \quad . \quad (3.56)$$

We have used here the fact that all rate constants are one and equations (3.51) and (3.53). The matrix  $\underline{\underline{A}}$  corresponding to this system is:





$$\underline{\underline{A}} = \begin{pmatrix} B - 1 & 4 \\ -B & 4 \end{pmatrix} \quad (3.57)$$

So the equation for the eigenvalues of  $\underline{\underline{A}}$  is:

$$\begin{vmatrix} w - B + 1 & -4 \\ +B & w + 4 \end{vmatrix} = 0 \quad (3.58)$$

The resulting dispersion equation is:

$$w^2 + w(5-B) + 4 = 0 \quad (3.59)$$

Using the Routh-Hurwitz conditions we find that the homogeneous steady-state solution is unstable to homogeneous perturbations if:

$$B > 5 \quad (3.60)$$

Now let us consider the stability of the homogeneous solution with respect to inhomogeneous perturbations. We write for the perturbed solutions:

$$\begin{aligned} X_1 &= X_{10} + \bar{\psi}_1(t) \\ X_2 &= X_{20} + \bar{\psi}_2(t) \\ Y_1 &= Y_{10} + \bar{\phi}_1(t) \\ Y_2 &= Y_{20} + \bar{\phi}_2(t) \end{aligned} \quad (3.61)$$



For inhomogeneous perturbations we require  $\bar{\psi}_1(t) \neq \bar{\psi}_2(t)$  and  $\bar{\phi}_1(t) \neq \bar{\phi}_2(t)$ . We now substitute (3.61) into (3.50), linearize, and use equations (3.51) and (3.53) as well as the fact that the rate constants are one. This yields:

$$\left. \begin{aligned} \frac{d\bar{\psi}_1}{dt} &= (B-1)\bar{\psi}_1 + 4\bar{\phi}_1 + (\bar{\psi}_2 - \bar{\psi}_1) \\ \frac{d\bar{\psi}_2}{dt} &= (B-1)\bar{\psi}_2 + 4\bar{\phi}_2 - (\bar{\psi}_2 - \bar{\psi}_1) \end{aligned} \right\} \quad (3.62)$$

$$\left. \begin{aligned} \frac{d\bar{\phi}_1}{dt} &= B\bar{\psi}_1 - 4\bar{\phi}_1 + D_y(\bar{\phi}_2 - \bar{\phi}_1) \\ \frac{d\bar{\phi}_2}{dt} &= B\bar{\psi}_2 - 4\bar{\phi}_2 - D_y(\bar{\phi}_2 - \bar{\phi}_1) \end{aligned} \right\} \quad (3.63)$$

Equations (3.62) can be combined to give one equation for  $(\bar{\psi}_2 - \bar{\psi}_1)$ . A similar arrangement can be performed with equation (3.63). Thus we obtain:

$$\begin{aligned} \frac{d(\bar{\psi}_2 - \bar{\psi}_1)}{dt} &= (B - 3)(\bar{\psi}_2 - \bar{\psi}_1) + 4(\bar{\phi}_2 - \bar{\phi}_1) \\ \frac{d(\bar{\phi}_2 - \bar{\phi}_1)}{dt} &= B(\bar{\psi}_2 - \bar{\psi}_1) - (4 + 2D_y)(\bar{\phi}_2 - \bar{\phi}_1) \end{aligned} \quad (3.64)$$

We now use the system of equations given by (3.64) to determine the matrix  $\underline{\underline{A}}$ . It is easy to see that the equation for the eigenvalues of  $\underline{\underline{A}}$  is given by:



$$\begin{vmatrix} w - B + 3 & -4 \\ B & w + 4 + 2D_y \end{vmatrix} = 0 \quad (3.65)$$

From this we obtain the following dispersion equation:

$$w^2 + w(7 - B + 2D_y) + 6D_y + 12 - 2BD_y = 0 \quad (3.66)$$

Using the Routh-Hurwitz conditions we see that the homogeneous steady-state solution is unstable with respect to inhomogeneous perturbations if:

$$B > 7 + 2D_y \quad (3.67a)$$

or

$$B > B_c = \frac{3D_y + 6}{D_y} \quad (3.67b)$$

Which of these is reached first will, of course, depend on the value of  $D_y$ . However, before (3.67a) is satisfied the homogeneous steady-state solution would become unstable with respect to homogeneous fluctuations. (See equation (3.60)).

Next we shall look at the stability of inhomogeneous steady-state solutions to the kinetic equations. In this case it is impossible to simplify the analysis and we must consider a fourth order dispersion equation. Using equations (2.7) and (2.31) we obtain:



$$\begin{vmatrix} w-2X_{10}Y_{10}+B+2 & -1 & -X_{10}^2 & 0 \\ -1 & w-2X_{20}Y_{20}+B+2 & 0 & -X_{20}^2 \\ 2X_{10}Y_{10}-B & 0 & w+X_{10}^2+D_y & -D_y \\ 0 & 2X_{20}Y_{20}-B & -D_y & w+X_{20}^2+D_y \end{vmatrix} = 0 \quad (3.68)$$

Here  $X_{10}$  ,  $X_{20}$  ,  $Y_{10}$  ,  $Y_{20}$  is a solution to the set of equations given by (3.52). These equations must be solved numerically for given values of  $B$  and  $D_y$  (using the values already specified for the rate constants,  $A$  and  $D_y$  ). Then equation (3.68) can be solved to determine the stability of the solution or the dispersion equation can be obtained from (3.68) and the Routh-Hurwitz conditions used to check for stability.

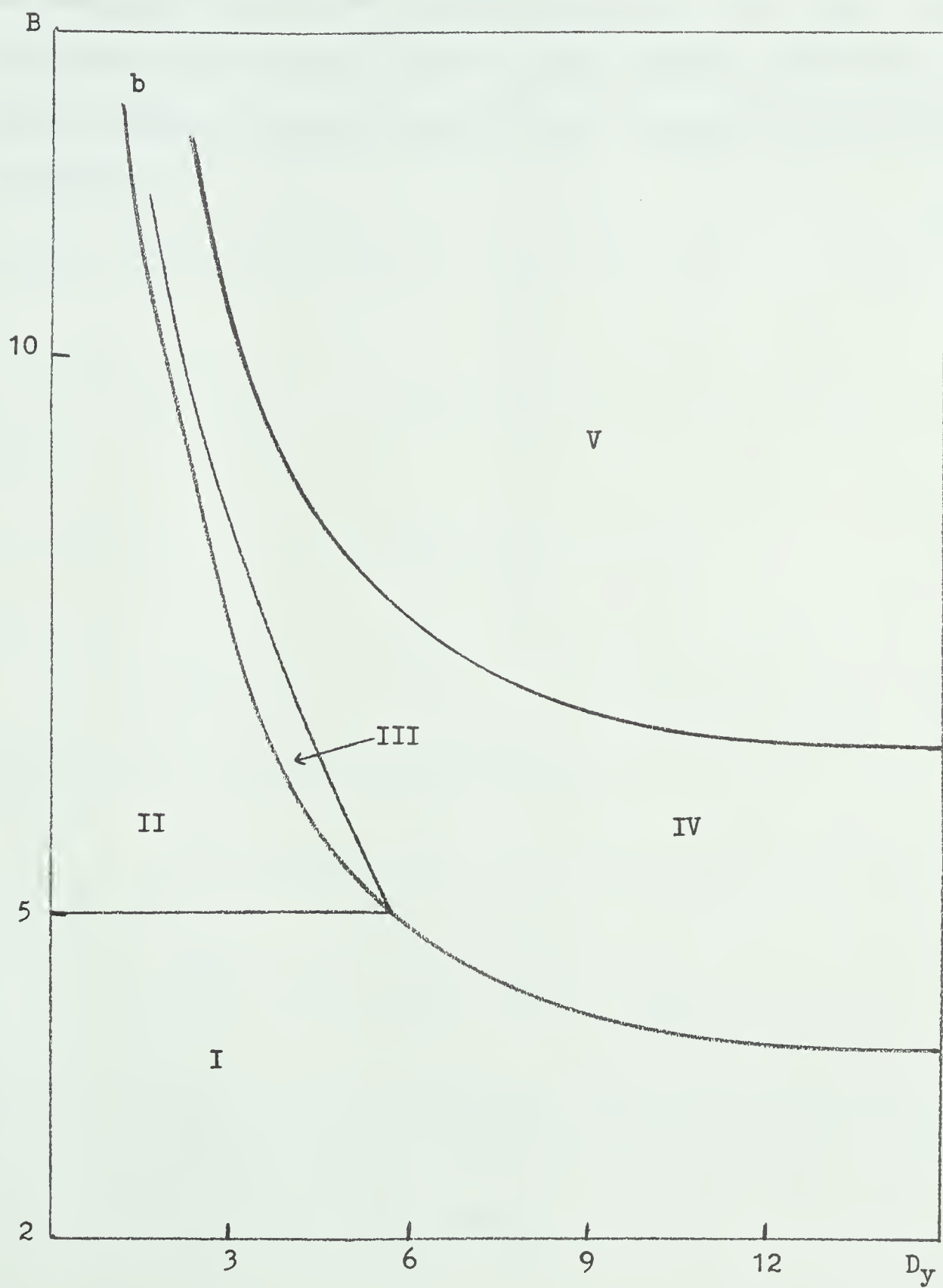
Lefever has carried out the numerical analysis and his results are shown in Figure 2. We quote from his paper to describe Figure 2<sup>13</sup>. "The homogeneous steady-state is stable in domain I. It becomes unstable with respect to inhomogeneous perturbations beyond the curve  $b$  . [It is also unstable for  $B > 7 + D_y$  . Lefever apparently did not consider this latter possibility and so did not draw in the appropriate line.] In regions II, III, and V no time-independent stable state exists. On the contrary, in region IV the inhomogeneous steady-state is stable.... This region corresponds therefore to what was called a dissipative structure."

In this chapter we have reviewed the works of Prigogine, Lefever, and Nicolis which show that the homogeneous steady-state solution to the chemical rate equations can become unstable with respect to spatial fluctuations. This implies that the stable solution, if there is one, may be space





FIGURE 2





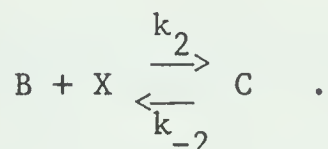
dependent. We have also reviewed the work of Lefever on the two box model which provides further strong evidence for the existence of a space structure. In addition, the importance of the boundary conditions was examined, which had not been done previous to this paper. An example was presented which showed that the type of boundary conditions imposed on the system can determine whether or not a symmetry breaking transition is possible.



## CHAPTER 4

### MULTIPLE STEADY-STATES

So far the chemical rate equations have had only one steady-state homogeneous solution. However, since the equations are non-linear, it is possible to have more than one solution. The following simple mechanism exhibits this phenomena and we will study it in detail:



We wish to look at this system in the two box model. Using this model, the chemical rate equations are:

$$\frac{dX_1}{dt} = AX_1^2 - k_{-1}X_1^3 - BX_1 + C + D_x(X_2 - X_1) \quad (4.2)$$

$$\frac{dX_2}{dt} = AX_2^2 - k_{-1}X_2^3 - BX_2 + C + D_x(X_1 - X_2) \quad .$$

For the time being we will designate any homogeneous steady-state solution by  $X_0$ . We will now study its stability. Using equations (2.7) and (2.31) we obtain the following equation:



$$\begin{vmatrix} w - 2AX_0 + 3k_{-1}X_0^2 + B + D_x & -D_x \\ -D_x & w - 2AX_0 + 3k_{-1}X_0^2 + B + D_x \end{vmatrix} = 0 \quad (4.3)$$

This can be rewritten as:

$$\begin{aligned} & w^2 + 2w(B + D_x + 3k_{-1}X_0^2 - 2AX_0) \\ & + (B + 3k_{-1}X_0^2 - 2AX_0 + D_x)^2 - D_x^2 = 0 \quad . \end{aligned} \quad (4.4)$$

Using the Routh-Hurwitz conditions we see that the conditions for stability are :

$$B + 3k_{-1}X_0^2 - 2AX_0 > -D_x \quad (4.5a)$$

$$B + 3k_{-1}X_0^2 - 2AX_0 > -2D_x \quad (4.5b)$$

$$B + 3k_{-1}X_0^2 - 2AX_0 > 0 \quad . \quad (4.5c)$$

If (4.5c) is satisfied the other two will automatically be satisfied. So equation (4.5c) is the only equation we will have to consider in the stability analysis of a homogeneous steady-state solution.

To find the homogeneous steady-state solution we need to solve the following equation for  $X_0$  :

$$k_{-1}X_0^3 - AX_0^2 + BX_0 - C = 0 \quad . \quad (4.6)$$





Since this is a cubic equation there are three roots possible, thus allowing multiple steady-states. In its present form equation (4.6) is difficult to solve. To facilitate solving it we will introduce the parameters  $a$  ,  $c$  ,  $d$  , and  $e$  , through the following implicit equations:

$$k_{-1} = c \quad (4.7a)$$

$$A = ac + d \quad (4.7b)$$

$$B = e + ad \quad (4.7c)$$

$$C = ea \quad (4.7d)$$

Now equation (4.6) may be written as:

$$(X_0 - a)(cX_0^2 - dX_0 + e) = 0 \quad (4.8)$$

The solutions to this equation are immediate. We find:

$$X_0 = a \quad (4.9a)$$

$$X_{0+} = \frac{+d + \sqrt{d^2 - 4ce}}{2c} \quad (4.9b)$$

$$X_{0-} = \frac{+d - \sqrt{d^2 - 4ce}}{2c} \quad (4.9c)$$

Depending on the choice of parameters  $c$  ,  $d$  , and  $e$  , only (4.9a) may be real and positive and thus physically meaningful or all three of the solutions may be meaningful.



Now we will use condition (4.5c) to study the stability of these three solutions. It is convenient to use equations (4.7) to rewrite condition (4.5c). It becomes:

$$e + ad + 3cX_0^2 - 2(ac+d) X_0 > 0 \quad . \quad (4.10)$$

First let us test the stability of the  $X_0 = a$  solution. We obtain:

$$e - ad + ca^2 > 0 \quad . \quad (4.11)$$

This is a quadratic equation in  $a$ . The stability condition (4.11) may be rewritten as the following two equations:

$$a > \frac{d + \sqrt{d^2 - 4ec}}{2c} = X_{0+} \quad (4.12a)$$

$$a < \frac{d - \sqrt{d^2 - 4ec}}{2c} = X_{0-} \quad (4.12b)$$

Written this way we have the rather surprising result that as  $a$  is varied while  $d$ ,  $e$  and  $c$  are held constant, the solution  $X_0 = a$  becomes unstable as it passes through the values of the other two homogeneous steady-state solutions.

Now we will consider the stability of the solution:

$$X_{0+} = \frac{d + \sqrt{d^2 - 4ec}}{2c} \quad .$$

This solution comes from solving:



$$cX_{0+}^2 - dX_{0+} + e = 0 \quad . \quad (4.13)$$

Rearranging gives us:

$$cX_{0+}^2 = dX_{0+} - e \quad . \quad (4.14)$$

Substituting this into condition (4.10) yields:

$$-X_{0+}d + 2e - da + 2X_{0+}ca < 0$$

or

$$a(2X_{0+}c - d) < X_{0+}d - 2e \quad . \quad (4.15)$$

Substituting for  $X_{0+}$  gives:

$$a < \frac{d^2 + d\sqrt{d^2 - 4ec} - 4ec}{2c\sqrt{d^2 - 4ec}} = X_{0+} \quad . \quad (4.16)$$

In a similar way we find that the condition for stability of the  $X_{0-}$  solution is:

$$a > X_{0-} \quad . \quad (4.17)$$

Thus we see that when  $d$ ,  $e$ , and  $c$  are chosen such that three solutions are possible, the stability of each solution is determined by the value of  $a$  with respect to  $d$ ,  $e$ ,  $c$ . It is quite interesting that just as one solution becomes unstable, another becomes stable. By looking at equations (4.12), (4.16), and (4.17) we see that there are



always two stable solutions. (The question of stability cannot be discussed if  $a = X_{0+}$  or if  $a = X_{0-}$  (See equations 4.12.) because then the theorem that assured us our linearization process was valid no longer applies.)

The solution  $X_0 = a$  is of particular importance because it is the solution at thermodynamic equilibrium. At equilibrium the rates of forward and backward reactions are equal. That is:

$$A X_e^2 = k_{-1} X_e^3 \quad (4.18a)$$

and

$$B X_e = C \quad (4.18b)$$

Thus:

$$X_e = \frac{A}{k_{-1}} = \frac{C}{B} \quad (4.19)$$

Using equations (4.7) we have:

$$X_e = \frac{ea}{e + ad} = \frac{ac + d}{c} \quad (4.20)$$

This can be satisfied only if:

$$d = 0 \quad (4.21a)$$

$$X_e = a \quad (4.21b)$$

Equation (4.21a) assures us that there is only one physically meaningful





solution since the other two will now be imaginary quantities. Because of the physical significance of the  $X_0 = a$  solution, it is not too surprising that the parameter  $a$  seems to play such an important role in the stability conditions.

After mechanism (4.1) had shown that there could exist multiple steady-state homogeneous solutions to kinetic equations, another example done by Edelstein appeared in the literature<sup>22</sup>. This example also introduced the multiple solutions through a cubic equation, but the mechanism governing the system contained two intermediate species instead of only one as considered in this paper.

Mechanism (4.1) also allows us to illustrate another interesting phenomenon. In the previous chapter the existence of a spatially dependent solution was shown by proving that the homogeneous steady-state solution could become unstable. However, it may also be possible for a non-homogeneous solution to be stable simultaneously with a homogeneous steady-state solution<sup>5</sup>. If this happened, the actual state of the system would be determined by the initial conditions imposed on the system. Different initial conditions could conceivably lead to different stable states. We will show that with the two box model it is possible to have a homogeneous steady-state stable solution and an inhomogeneous steady-state stable solution simultaneously. Because of the difficulty of solving analytically for the inhomogeneous steady-state solution we will give a numerical example.

The algebraic equations for an inhomogeneous steady-state solution are:



$$(X_{10} - a)(cX_{10}^2 - dX_{10} + e) = D_x(X_{20} - X_{10}) \quad (4.22)$$

$$(X_{20} - a)(cX_{20}^2 - dX_{20} + e) = -D_x(X_{20} - X_{10}) \quad .$$

First we must determine the criterion for stability of the inhomogeneous steady-state solution. By analogy with equation (4.3) we have:

$$\begin{vmatrix} w - 2AX_{10} + 3k_{-1}X_{10}^2 + B + D_x & -D_x \\ -D_x & w - 2AX_{20} + 3k_{-1}X_{20}^2 + B + D_x \end{vmatrix} = 0 \quad (4.23)$$

Expanding gives:

$$\begin{aligned} & w^2 + w(3k_{-1}X_{10}^2 + 2B + 2D_x - 2AX_{10} - 2AX_{20}) \\ & + (3k_{-1}X_{10}^2 + B + D_x - 2AX_{10})(3k_{-1}X_{20}^2 + B + D_x - 2AX_{20}) - D_x^2 = 0 \quad . \end{aligned} \quad (4.24)$$

Using the Routh-Hurwitz conditions and equation (4.7) we can write the conditions for stability as:

$$3c(X_{10}^2 + X_{20}^2) + 2e + 2ad - 2(ac+d)(X_{10} + X_{20}) + 2D_x > 0 \quad (4.25a)$$

$$(3cX_{10}^2 + e + ad + D_x - 2(ac+d)X_{10})(3cX_{20}^2 + e + ad + D_x - 2(ac+d)X_{20}) - D_x^2 > 0 \quad (4.25b)$$

We will choose the following values for our parameters:



$$D_x = 1 \quad ; \quad a = 2$$

(4.26)

$$d = +4c \quad ; \quad e = 3c-2$$

With these values it can easily be verified by substitution into equations (4.22) that an inhomogeneous steady-state solution is:

$$X_{10} = 1 \quad ; \quad X_{20} = 3 \quad .$$

(4.27)

Now we can use conditions (4.25) to test the stability of this solution.

We obtain the following:

$$c > \frac{1}{2}$$

(4.28a)

$$c > 1 \quad .$$

(4.28b)

Condition (4.28a) corresponds to (4.25a) and (4.28b) corresponds to (4.25b). Clearly by choosing  $c > 1$  we shall guarantee the stability of this inhomogeneous steady-state solution.

Using the values specified in equations (4.26) let us now look at the values of the corresponding homogeneous steady-state solution. We have:

$$X_0 = 2$$

(4.29a)

$$X_{0+} = \frac{4c + \sqrt{4c^2 + 8c}}{2c}$$

(4.29b)

$$X_{0-} = \frac{4c - \sqrt{4c^2 + 8c}}{2c} \quad .$$

(4.29c)



It can easily be shown that both  $X_{0+}$  and  $X_{0-}$  are positive valued for all  $c > 1$ . Thus for  $c > 1$ , all three homogeneous steady-state solutions are physically meaningful. By the previous work that we did, we know that two of them will be stable. It turns out that the solutions  $X_{0+}$  and  $X_{0-}$  are both stable for all  $c > 1$ , while the  $X_0 = 2$  solution is unstable. Thus we see that for this simple mechanism considered in the two box model it is possible to have a stable inhomogeneous steady-state solution simultaneously with a stable homogeneous steady-state solution. Indeed, because of the existence of multiple homogeneous steady-state solutions we have at least three simultaneously stable solutions - two homogeneous and at least one inhomogeneous solution.





## CHAPTER 5

### CONCLUSION

In this paper we have given evidence to support the proposition that a chemical system may under some circumstances exhibit spatial structure. Recently there has been reported an experimental confirmation of this in the literature. Herschkowitz-Kaufman<sup>8</sup> prepared a mixture of  $\text{Ce}_2(\text{SO}_4)_3$ ,  $\text{KBrO}_3$ ,  $\text{CH}_2(\text{COOH})_2$ ,  $\text{H}_2\text{SO}_4$ , and drops of Ferroine as a redox indicator. The mixture was made initially homogeneous by stirring and throughout the experiment the temperature was maintained constant at  $21^\circ\text{C}$ . When the stirring was stopped, the solution immediately showed oscillations in time; the color of the solution changed periodically from red to blue. After a number of time oscillations an inhomogeneity in the concentration appeared and gradually the solution arranged itself into alternating horizontal layers of red and blue. After about thirty minutes the system approached chemical equilibrium and again became homogeneous.

Several things should be noted about this experiment. An important one is that the spatial structure formed would tend to support the applicability of the derivative boundary conditions, not the fixed boundary conditions. For fixed boundary conditions, the concentrations of the various species would have had to remain constant at the walls of the container. Alternating layers which extend to the boundary preclude this possibility. On the other hand, the horizontal layers indicate that the normal derivative of the concentration could be zero.



Further it is apparent from the description of the experiment, that the structure was not caused by an instability in the steady-state solution with respect to spatial fluctuations. If this were the case the structure would have appeared immediately after the cessation of stirring, instead of being preceded by a period of temporal oscillations. It is possible that the steady-state solution was unstable initially with respect to homogeneous fluctuations and so evolved into a time dependent solution which then became unstable with respect to inhomogeneous fluctuations. It could also be that this experiment is an example of the phenomena discussed in the fourth chapter. That is, no instability at all is involved, but there is simply a structured state which is stable and with the given initial conditions the system evolved into this state. Obviously, further experimental and theoretical work is needed to decide which, if any, of these possibilities is correct in order to explain the appearance of this dissipative structure.

In conclusion, it should be mentioned that it seems that this area of research could be of great interest in biology. It has been shown that the type of mechanism which can lead to instabilities is consistent with the mechanisms established for several biological processes<sup>17</sup>. Since the biological world seems governed by structure (for example, the cell and organized groups of cells), this could provide a clue in explaining the appearance and maintenance of this structure. Already the concept of dissipative instability has been used in a model of a membrane<sup>3</sup>. It is to be expected that further applications will appear in the literature.



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